# Electron emission and defect formation in the interaction of slow, highly charged ions with diamond surfaces

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We report on electron emission and defect formation in the interaction between slow ($v \approx 0.3\ v_{Bohr}$) highly charged ions (SHCI) with insulating (type IIa) and semiconducting (type IIb) diamonds. Electron emission induced by $^{31}P^{q+}$ (q=5 to 13), and $^{136}Xe^{q+}$ (q=34 to 44) with kinetic energies of 9 kV×q increase linearly with the ion charge states, reaching over 100 electrons per ion for high xenon charge states without surface passivation of the diamond with hydrogen. Yields from both diamond types are up to a factor of two higher then from reference metal surfaces. Crater like defects with diameters of 25 to 40 nm are formed by the impact of single $Xe^{44+}$ ions. High secondary electron yields and single ion induced defects enable the formation of single dopant arrays on diamond surfaces.

## I. Introduction

Electron emission and defect formation in diamond have recently received increased attention due to reports of unusually high electron emission yields from hydrogen passivated diamond surfaces [1, 2], and the demonstration of rudimentary quantum information processing with NV defect centres [3]. The fabrication of device structures with arrays of coupled defect complexes requires poses a significant challenge [4, 5]. Ion implantation allows placement of ions into desired locations via focused ion beam or scanning probe alignment techniques [6-8]. Single defect centre array formation requires a method for single ion detection, such as detection of secondary electrons, and a detailed understanding of defect formation dynamics [9, 10].

Secondary electron emission and surface defect formation in the interaction of slow ($v < v_{Bohr}$) highly charged ions with surfaces is dominated by the deposition of potential energy of the ions (the sum of the binding energies of the electrons that were removed to form the ions). Due to neutralization and relaxation on a 10 fs time scale, most of the potential energy is deposited within a few nm of the sample surface and effective energy deposition rates can exceed $\sim 10^{13}$ W/cm$^2$ [11, 12]. In this article, we report on studies of electron emission and defect formation in the interaction of slow, highly charged phosphorus (5+ to 13+) and xenon (34+ to 44+) ions with diamond surfaces. This study is motivated by the interest in formation of optically active defects in ordered arrays via ion implantation. We find that high electron emission yields and single ion induced defects that can be imaged *in situ* with a scanning probe are two promising techniques for defect and dopant array formation on diamond surfaces.

## II. Experimental setup

Ions were extracted from the Electron Beam Ion Trap (EBIT) at Lawrence Berkeley National Laboratory [13], and reached the target chamber after momentum analysis in a 90° bending magnet. The pressure in the target chamber was in the low $10^{-8}$ torr range. We emphasize that this study focuses on the applied aspect of electron emission and defect formation under modest vacuum conditions as they are present in typical ion implanters, and not on atomically clean surfaces prepared under ultra-high vacuum conditions. Ion energies, $E_{kin} = q \times (U_{ext} + U_{sample})$ were set by the EBIT extraction potential $U_{ext}$=8 kV and a negative sample bias of 1 kV during electron emission measurements. Contributions to the observed emission yields from kinetic electron emission can be estimated from the low charge state data and amount to a few electrons per ion, compared to over 100 electrons/ion for highly charged xenon ions. Effects of varying kinetic energies on electron emission yields have previously been found to be negligible for highly charged ions, since the potential energy that is deposited close to the surface exceeds the deposition of kinetic energy from inelastic and elastic collisions [12, 14]. We used a sputter cleaned aluminium target as a reference material. Ions impinged on targets under normal incidence. Typical ion currents were below one particle pA ($<10^6$ ions/s). We observed no macroscopic sample charging, and total fluences were below $10^{10}$ cm$^{-2}$. Secondary electrons were detected in an annular microchannel plate detector [14], where the detected pulse height is proportional to the number of electrons emitted by individual ions. Emission yields were

calibrated by comparison to literature data [11, 12, 14].

Electron emission was measured for relatively rare natural diamonds of type IIb (semiconducting, p-type) and type IIa (insulating) which both have low nitrogen concentrations. Type IIb diamonds are p-type semiconducting due to naturally occurring, uncompensated boron acceptors. Investigation of topological defects formed on the diamond surface by ion impacts required preparation of flat surfaces. The required flatness could not be achieved by state-of-the-art diamond polishing techniques. Among the different methods attempted, molecular bombardment gave the finest results with a roughness of the order of approximately 30 nm. In order to improve on that, a type IIa diamond was aligned with an ablation laser along the [111] crystallographic direction where a small indentation was formed. This indentation acted as guide to lead a chisel for a precise cleavage along the (111) plane. The cleaved surface produced in this manner exhibits few hundred nanometer terraces with an RMS roughness of about 1 nm, adequate for the present analysis (see Figure 2 below).

## III. Electron emission

Electron emission yields from a type IIb (semiconducting) diamond, a type IIa (insulating) diamond and the aluminium reference target are shown as a function of ion charge state Figure 1. No surface passivation with hydrogen was applied. Yields form both diamond types are higher then yields from the reference metal sample. This is in contrast to studies of thin $SiO_2$ films on silicon , which showed suppressed electron emission compared to metal surfaces [14]. Provided that macroscopic charging is avoided, electron emission yields in kinetic electron emission are typically higher from insulators then from metals [15]. This has been attributed to lower surface electron affinities for the escape of excited electrons from the insulators compared to metal work functions, and to the longer inelastic mean free paths of energetic electrons along their escape path inside the material. In an earlier study with SHCI, lower yields from $SiO_2$ films were attributed to a local effective work function increase where the low mobility holes left behind after a number of electrons have escaped form an attractive potential, suppressing escape of the following electrons [14]. Our finding of higher emission yields from diamond compared to metal surfaces indicates that local charging in the course of a single ion impact is compensated by higher hole mobilities of 100 $cm^2$/Vs for diamond vs. $<10^{-4}$ $cm^2$/Vs for $SiO_2$ [16]. Do to the low fluences applied here, we were not able to probe the recently detailed hole trapping effect on electron emission from poly-crystalline diamond surfaces [17].

Electron emission yields increase linearly with the incident ion charge state, consistent with previous findings for a series of materials [11, 12, 14], and well described by a classical-over-the-barrier model of electron capture, hollow atom formation and decay by a series of di-electronic processes [19]. We find that electron yields form the insulating diamond were consistently higher compared to the semiconducting diamond and attribute this tentatively to a slightly larger inelastic mean free path that allows secondary electrons to escape from a slightly larger volume in the type IIa compared to the type IIb diamond.

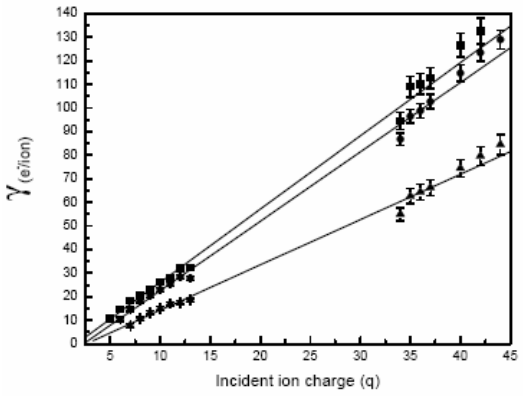


Figure 1. Electron emission yields as a function of ion charge, q. The plots show yields for a type IIa diamond (■), a type IIb diamond (●) and an aluminium reference target (▲) for phosphorous, and xenon ions. Solid lines are linear fits to the data.

## IV. Ion induced defects on diamond surfaces

Flat type IIa diamonds were irradiated at normal incidence with about $Xe^{44+}$ (dose = $10^{10}$ ions/$cm^2$, $E_{kin}$=352 keV). After exposure, samples were analyzed *ex situ* by Atomic-Force Microscopy (AFM). The formation of craters by individual ion impacts was observed. Figure 2 shows a contact AFM image with craters exhibiting diameters ranging from 25 to 40 nm.

The crater size is smaller then defect sizes found for self assembled monolayer films on silicon [19] and larger then the sizes of blisters formed on mica surfaces by similar ions [20]. Several models of potential sputtering or electronic sputtering by SHCI have been proposed to describe sputtering rates from insulators ($UO_2$, LiF, $SiO_2$) and semiconductors (Si, GaAs) [11, 12, 21] in the

interaction with SHCI. Simulations by Yamamura et al. predict a tenfold increase of the sputtering yield of diamond for $Xe^{44+}$ impact [22], and a detailed time evolution of the impact of low energy $Xe^{44+}$ ions with a diamond surface was presented. Increased sputtering resulted from the Coulomb explosion associated with the high levels of induced charge in a small surface near target volume. While a phenomenological Coulomb explosion model is intuitive considering large electron emission yields we point out that more detailed studies will be necessary to delineate sputtering and surface damage mechanisms.

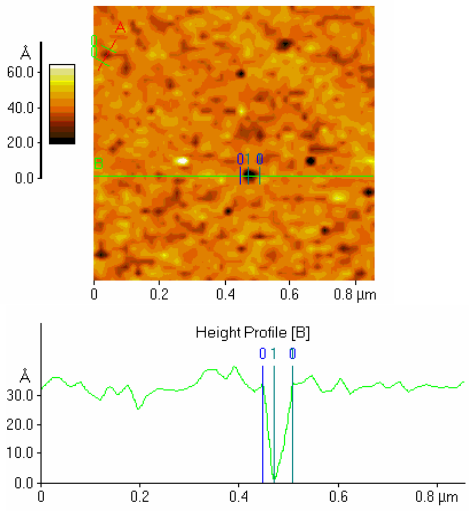


Figure 2. AFM images of defects on the surface of a "flat" diamond type IIa surface induced by single $Xe^{44+}$ ions.

We point out that the defects induced by single ion impacts are rather easy to observe by AFM, making them promising features to signify single ion implantation.

## V. Conclusions

Electron emission induced by slow, highly charged ions from diamond surfaces was found to be higher then for metal reference targets and reached over 100 electrons for highly charged xenon ions without need for surface passivation with hydrogen. Single ion impact induced structural defects are observed with crater diameters of 25 to 40 nm from impact of $Xe^{44+}$ ions. High electron emission yields from diamond surfaces make detection of single, highly or multiply charged ion impacts easier for applications in single atom array formation, without requiring surface passivation with hydrogen. *In situ* detection of single ion impacts is possible also by repeated imaging of a selected area and sensing of topological modifications from a single ion impact event after a selected dwell time.


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## References


[1] E. Chelfetz, V. Richter, N. Koenigsfeld, and R. Kalish, J. Appl. Phys. 92, 7611 (2002)
[2] D. I. Hoxley, D. N. Jamieson, S. Prawer, V. Richter, and R. Kalish, Nucl. Instr. Meth. B (2002)
[3] F. Jelezko, T. Gaebel, I. Popa, M. Domhan, A. Gruber, J. Wrachtrup, Phys. Rev. Lett. 93, 130501 (2004)
[4] J. Meijer, et al., Applied Phys. A 83, 321 (2006)
[5] P. Hemmer, et al., Proc. Spie Vol. 6130, 0E-1 (2006)
[6] T. Shinnada, S. Okamoto, T. Kobayashi, and S. Ohdimari, Nature 437, 1128 (2005)
[7] A. Persaud, et al., NanoLetters 5, 1087 (2005)
[8] D. N. Jamieson, et al., Appl. Phys. Lett 86, 202101 (2005)
[9] J. Meijer, et al., Appl. Phys. Lett. 87, 261909 (2005)
[10] J. R. Rabeau, et al, Appl. Phys. Lett. 88, 023113 (2006)
[11] A. Arnau, et al., Surf. Sci. Rep. 27, 113 (1997)
[12] T. Schenkel, A. V. Hamza, A. V. Barnes, and D. H. Schneider, Prog. Surf. Sci. 61, 23 (1999)
[13] T. Schenkel et al., Rev. Sci. Instr. 73, 663 (2002)
[14] T. Schenkel, A.V. Barnes, M.A. Briere, A.V. Hamza, A. Schach von Wittenau, D.H. Schneider, Nucl. Inst. Meth. Phys. Res. B 125 (1997) 153
[15] D. Hasselkamp, Particle induced electron emission II, in G. Hoehler (ed.), Springer Tracks in Modern Physics, Vol. 123 (Springer, New York, 1992)
[16] H. Jacobsson and G. Holmén, Phys. Rev. B 49, 1789–1795 (1994)
[17] S. Prawer, S. Rubanov, S. M. Hearne, D. N. Jamieson, and R. Kalish, Phys. Rev. B 73, 153202 (2006)

[18] J. Burgdorfer, P. Lerner and F.W. Meyer, Phys. Rev. A 44, 5674 (1991)
[19] T Schenkel, M. Schneider, M. Hattass, M. W. Newman, A. V. Barnes, A. V. Hamza, D.H. Schneider, R. L. Cicero, C. E. D. Chidsey, J. Vac. Sci. Technol. B 16, 3298 (1998)
[20] C. Rühlicke, M. A. Briere, and D. H. Schneider, Nucl. Instr. Meth. B 99, 528 (1995)
[21] F. Aumayr, and H.-P. Winter, Phil. Trans. R. Soc. Lond A 362, 77 (2004)
[22] Y. Yamamura, S. T. Nakagawa, and H. Tawara, Nucl. Instr. Meth. B 98, 400 (1995)